

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 108 681 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
20.06.2001 Bulletin 2001/25

(51) Int Cl.7: **C01G 45/00**(21) Application number: **00123846.8**(22) Date of filing: **02.11.2000**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**
Designated Extension States:
AL LT LV MK RO SI

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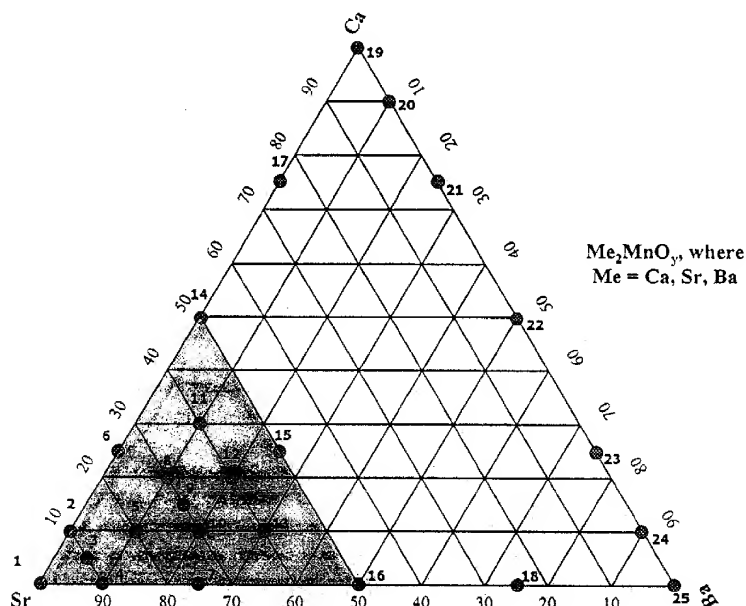
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(54) **Alkaline earth-manganese oxide pigments**

(57) Alkaline earth-manganese oxides are used as pigments. The alkaline earth-manganese oxide pigments are preferably of the formula Me_xMnO_y , where Me is at least one metal selected from Ca, Sr, Ba and Mg, x is from 0.01 to 99, and y is greater than or equal to x + 1 and less than or equal to x + 2. The pigments are useful as colorants, and also possess improved re-

flectance characteristics, particularly in the IR region, and may reduce IR-induced heat buildup. These colorants can be used to form colored objects, or coat objects when they are either added into or applied onto materials such as paints, inks, plastics, glasses, ceramics and the like. The patent also covers the production of these pigments.

**FIG. 1**

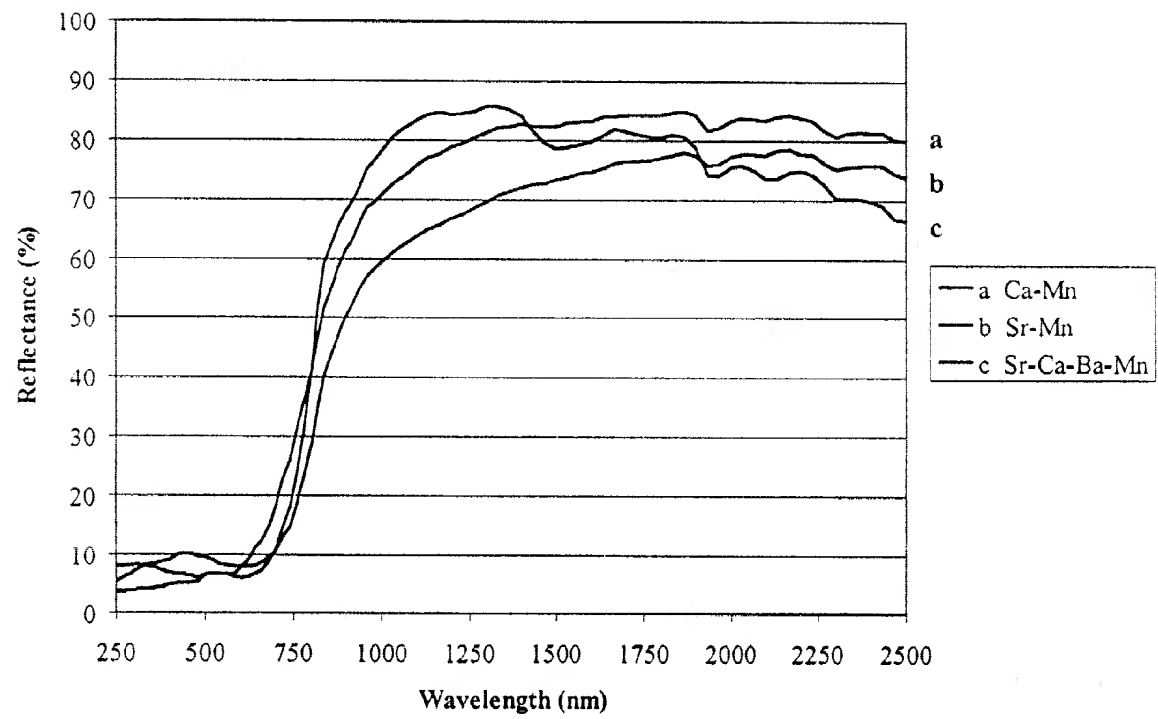


FIG. 8

DescriptionFIELD OF THE INVENTION

5 **[0001]** The present invention relates to pigments for plastics, glasses, ceramics, paints, enamels, inks and other types of materials, and more particularly relates to the use of alkaline earth-manganese oxide compositions as pigments for use in plastics, paints, coatings, glass enamels and other materials.

BACKGROUND INFORMATION

10 **[0002]** Pigments are widely used in various applications such as paints, inks, plastics, rubbers, ceramics, enamels and glasses. There are various reasons for using inorganic pigments. Among these are the coloristic properties of the pigments, their visible as well as ultraviolet (UV) and infrared (IR) reflectance characteristics, their light fastness and their high temperature stability, which is necessary when the objects being colored are formed at elevated temperatures.

15 A summary of many types of inorganic pigments and some of their applications can be found in the Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Volume 18.

[0003] Manganese is used as a chromophore in several mixed metal oxide pigments, which are listed in the Dry Color Manufacturers Association (DCMA) classifications. In the corundum structure, manganese is used to form manganese alumina pink corundum, DCMA number 3-04-5. Manganese is also used as a chromophore in the rutile structure to form brown pigments, such as manganese antimony titanium buff rutile (DCMA 11-20-6), manganese chrome antimony titanium brown rutile (DCMA 11-46-7), and manganese niobium titanium brown rutile (11-47-7). Manganese is also a component in many spinel pigments to form brown or black colors. Examples are manganese ferrite black spinel (DCMA 13-41-9), chrome iron manganese brown spinel (DCMA 13-48-7), and chrome manganese zinc brown spinel (DCMA 13-51-7).

25 **[0004]** Currently, several of the DCMA classified pigments are used due to their IR reflectance performance. The IR reflective performance is typically determined by the relative amount of reflectance provided in the solar infrared region of the spectrum, i.e., 700 to 2,500 nm in wavelength, compared to the visible region of the spectrum, i.e., 400 to 700 nm in wavelength. Common black pigments such as carbon black have low reflectances in both regions. To obtain enhanced IR reflectance, inorganic black pigments from the classification DCMA 13-50-9, chrome iron nickel black spinel, or DCMA 3-05-3, chrome green black spinel, are used for these applications. The pigment DCMA 13-30-3, cobalt chromite green spinel, also provides a higher IR reflectance than visible reflectance.

30 **[0005]** The above-mentioned pigments do not provide the desired color values, contain the desired chemistry or provide the desired infrared reflectance properties for many applications. The present invention provides pigments with enhanced color, composition and performance characteristics.

SUMMARY OF THE INVENTION

35 **[0006]** This invention relates to pigments that can be represented by the formula Me_xMnO_y , where Me comprises at least one metal of the alkaline earth metals Ca, Ba, Sr and Mg, x ranges from 0.01 to 99, and y designates the number of oxygen atoms required to maintain electroneutrality. Preferably, x ranges from 0.08 to 12, more preferably from 0.25 to 4, and y ranges from x + 1 to x + 2. These pigments can be used to color objects, or coat objects by their use in applications such as paints, inks, plastics, glasses, ceramics and the like. The invention also includes the production of these pigments, substitution of other elements into these pigments, and the use of protective coatings on these pigments in order to enhance their properties.

40 **[0007]** In accordance with an embodiment of the present invention, one property of the alkaline earth-manganese oxide pigments is high infrared reflectance while maintaining a visibly dark color. This high infrared reflectance may result in substantially less heat buildup in colored objects using the present alkaline earth-manganese oxide pigments.

[0008] Another property of the present alkaline earth-manganese oxide pigments is their ability to change to a different color when exposed to high temperatures. For example, when surfaces containing these materials are subjected to elevated temperatures by laser marking, legible marks are obtained.

50 **[0009]** Another aspect of the present invention is to provide a coating composition including a liquid carrier and a pigment comprising alkaline earth-manganese oxide dispersed therein.

[0010] Another aspect of the present invention is to provide an article including a substrate matrix and alkaline earth-manganese oxide pigment dispersed in the matrix.

55 **[0011]** A further aspect of the present invention is to provide an article including a substrate and a coating comprising an alkaline earth-manganese oxide pigment covering at least a portion of the substrate.

[0012] Another aspect of the present invention is to provide a method of making an alkaline earth-manganese oxide pigment. One method includes the steps of mixing powders capable of yielding metal oxides, and calcining the mixture.

[0013] These and other aspects of the present invention will be more apparent from the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Fig. 1 is a graph illustrating the mole percentages of Ca, Sr and Ba contained in several alkaline earth-manganese oxide pigments of the formula Me_2MnO_4 in accordance with embodiments of the present invention.

[0015] Fig. 2 is a graph illustrating masstone visible and infrared reflectance characteristics for black Sr-Mn-O and Ca-Mn-O pigments of the present invention in comparison with conventional Cr-Fe-O, Ni-Mn-Cr-Fe-O and carbon black pigments.

[0016] Fig. 3 is a graph illustrating tint visible and infrared reflectance characteristics for black Sr-Mn-O and Ca-Mn-O pigments of the present invention in comparison with conventional Cr-Fe-O, Ni-Mn-Cr-Fe-O and carbon black pigments.

[0017] Fig. 4 is a graph illustrating masstone visible and infrared reflectance characteristics for brown Ca-Mn-O and Ba-Mn-O pigments of the present invention in comparison with conventional Mn-Sb-Ti-O and Cr-Fe-Zn-O pigments.

[0018] Fig. 5 is a graph illustrating tint visible and infrared reflectance characteristics for brown Ca-Mn-O and Ba-Mn-O pigments of the present invention in comparison with conventional Mn-Sb-Ti-O and Cr-Fe-Zn-O pigments.

[0019] Fig. 6 is a graph illustrating masstone visible and infrared reflectance characteristics for green Sr-Mn-O, Ca-Sr-Ba-Mn-O and Ba-Mn-O pigments of the present invention in comparison with a conventional Co-Cr-Zn-Ti-O pigment.

[0020] Fig. 7 is a graph illustrating tint visible and infrared reflectance characteristics for green Sr-Mn-O, Ca-Sr-Ba-Mn-O and Ba-Mn-O pigments of the present invention in comparison with a conventional Co-Cr-Zn-Ti-O pigment.

[0021] Fig. 8 is a graph illustrating masstone visible and infrared reflectance characteristics at wavelengths of up to 2,500 nm for Ca-Mn-O, Sr-Mn-O and Ca-Sr-Ba-Mn-O pigments in paint applications in accordance with the present invention.

DETAILED DESCRIPTION

[0022] This invention relates to the use of alkaline earth-manganese oxides as pigments. The alkaline earth-manganese oxide pigments are of the formula Me_xMnO_y , where Me is at least one alkaline earth metal selected from Ca, Sr, Ba and Mg, x ranges from 0.01 to 99, and y designates the number of oxygen atoms required to maintain electroneutrality. Preferably, x ranges from 0.08 to 12, more preferably from 0.25 to 4. The value of y is preferably greater than or equal to x + 1 and less than or equal to x + 2.

[0023] Alkaline earth-manganese oxide materials of the above-noted formula have been found to possess favorable colorant properties, and are useful as pigments of various colors such as black, brown, green, etc. In addition to their use as colorants, the alkaline earth-manganese oxide pigments of the invention may provide improved infrared reflectance and reduced heat buildup properties. The pigments are useful in many applications, including organic chemical compositions such as plastics, rubbers and the like, coating compositions such as paints, printing inks and the like, and inorganic chemical compositions such as glass enamels, porcelain enamels and the like.

[0024] Table 1 provides concentrations of manganese in some pigments of the formula Me_xMnO_y relative to its corresponding alkaline earth metal in accordance with embodiments of the invention.

Table 1

Composition Ranges of Alkaline Earth Manganese Oxide Pigments			
Chemistry	Color	Preferred mol % Mn	More Preferred mol % Mn
Ca_2MnO_y	Black	10-40	20-33
$\text{Ca}_{0.5}\text{MnO}_y$	Brown	60-90	60-70
SrMnO_y	Black	45-60	45-55
Sr_2MnO_y	Green	20-45	33-40
BaMnO_y	Brown	45-90	45-60
Ba_2MnO_y	Green	10-45	25-40

[0025] It is also possible to produce pigments through the introduction of a second alkaline earth metal into pigments such as those listed in Table 1. In one embodiment of the invention, the alkaline earth-manganese oxide pigments comprise Me_2MnO_4 , where Me is at least one metal selected from Ca, Sr, Ba and Mg. As an example, the Sr_2MnO_y pigment can accommodate extensive amounts of both calcium and barium. Fig. 1 illustrates various mole percentages

of Ca, Sr and Ba in such Me_2MnO_4 pigments in accordance with this embodiment. Some preferred compositions are shown by the shaded region of Fig. 1.

[0026] Table 2 lists preferred concentrations of strontium in Me_2MnO_y relative to other alkaline earth metals.

Table 2

Composition Ranges of Alkaline Earth Metals in $(\text{Sr,Ca,Ba})_2\text{MnO}_y$			
Chemistry	Color	mol % Sr	Preferred mol % Sr
$(\text{Sr,Ca,Ba})_2\text{MnO}_y$	Brown	0-100	50-100

[0027] Color values of the pigments listed in Tables 1 and 2 are given in Table 3 (masstone polyvinyl chloride) and Table 4 (tint polyvinyl chloride). For Tables 3 through 5 below: L^* is lightness on a scale of 0 (black) to 100 (white); a^* indicates green (negative) or red (positive); b^* indicates blue (negative) or yellow (positive); C^* defines chroma ($C^* = (a^{*2} + b^{*2})^{1/2}$); and h is hue angle.

Table 3

Color Values (Masstone)						
Chemistry	Color	L^*	a^*	b^*	C^*	h
Ca_2MnO_y	Black	27.85	0.88	0.38	0.96	23.63
SrMnO_y	Black	29.41	0.91	-0.15	0.93	350.65
$\text{Ca}_{0.5}\text{MnO}_y$	Brown	29.60	5.90	1.17	6.01	11.25
BaMnO_y	Brown	36.58	3.45	11.85	12.35	73.75
Sr_2MnO_y	Green	31.90	-0.90	2.73	2.88	108.22
Ba_2MnO_y	Green	31.49	-1.12	5.20	5.32	102.17
$(\text{Sr,Ca,Ba})_2\text{MnO}_y$	Green	31.82	-1.60	3.65	3.99	113.72

Table 4

Color Values (Tint, Color Matched to Equal L^* value)						
Chemistry	Color	L^*	a^*	B^*	C^*	h
Ca_2MnO_y	Black	55.89	0.86	-2.80	2.93	286.99
SrMnO_y	Black	56.25	-0.16	-1.77	1.78	264.87
$\text{Ca}_{0.5}\text{MnO}_y$	Brown	54.89	6.29	-1.62	6.49	345.55
BaMnO_y	Brown	58.45	2.58	10.35	10.67	76.02
Sr_2MnO_y	Green	57.06	-2.07	1.34	2.47	147.00
Ba_2MnO_y	Green	57.17	-1.59	3.92	4.23	112.10
$(\text{Sr,Ca,Ba})_2\text{MnO}_y$	Green	57.51	-2.81	2.73	3.92	135.85

[0028] It is also possible to produce pigments through substitution of magnesium into pigments such as those listed in Table 1. For example, 4 wt% MgO was added into each alkaline earth-manganese oxide listed in Table 1. The resulting pigments, as set forth in Table 5, were not appreciably different in color (compare Tables 3 and 5) and were still IR reflecting (e.g., greater than 50% reflectance at 1,100 nm).

Table 5

Color Values (Masstone, Mg-doped pigments)						
Chemistry	Color	L^*	a^*	b^*	C^*	h
Ca_2MnO_y	Black	28.22	1.58	0.98	1.86	31.86

Table 5 (continued)

Color Values (Masstone, Mg-doped pigments)						
Chemistry	Color	L*	a*	b*	C*	h
SrMnO _y	Black	27.87	1.51	-0.51	1.59	341.36
Ca _{0.5} MnO _y	Brown	30.24	5.93	1.21	6.05	11.49
BaMnO _y	Brown	36.80	4.50	14.87	15.54	73.18
Sr ₂ MnO _y	Green	32.69	-0.22	5.02	5.03	92.51
Ba ₂ MnO _y	Green	33.69	-0.87	6.02	6.02	98.27

[0029] It is also possible to produce pigments through substitution of non-alkaline earth metals. For example, the addition of 4 wt% TiO₂ into Ba₂MnO_y yields a pigment that is still green and IR reflecting. The addition of 4.5 wt% V₂O₅ into Sr₂MnO_y yields a pigment that is still green and IR reflecting. The addition of 2 wt% ZrO₂ into BaMnO_y yields a pigment that is still brown and IR reflecting.

[0030] It is apparent that substitutions into these compositions can be made to enhance or otherwise modify their properties. Various dopants can be added in sufficient amounts such that they do not significantly adversely affect the performance of the pigment. Typically, the total amount of such dopants does not exceed 30 mol percent of the alkaline earth metal or manganese. These dopants include elements from Groups I-A, III-A, IV-A, V-A, VI-A, VII-A, VIII-A, I-B, II-B, III-B, IV-B, V-B, VI-B, VIII-B, the Lanthanide elements, and the Actinide elements of the Periodic Table.

[0031] The alkaline earth-manganese oxide pigments of the present invention may be formed by processes such as calcination techniques, sol-gel techniques, spray pyrolysis and/or chemical precipitation. Calcination is a particularly preferred process for making the present alkaline earth-manganese oxide pigments. Typically, the raw materials are oxides of the alkaline earths and of manganese, or compounds that will yield the desired oxides upon calcination. For example, manganese may be supplied as manganese dioxide or as manganese sesquioxide. Alternatively, manganese sulfate, carbonate or hydroxide are among the acceptable choices because, upon calcination, manganese oxide will result from calcining these raw materials.

[0032] The weight ratio of alkaline earth oxide or other alkaline earth compound to manganese oxide or other manganese compound is selected to produce the desired composition upon calcination. Mixing of the raw material should be sufficient to assure good physical contact between the different compounds present in order to assure good reaction during the calcination. This may be accomplished, for example, by grinding in a pebble mill either with or without the addition of water. It may also be adequate to hammer mill a simple mixture of the compounds present, or to mix them in a mortar and pestle.

[0033] The mixed powders are preferably calcined at temperatures of from about 500 to about 1,500°C, more preferably from about 900 to about 1,300°C. Calcination times of from about 1 to about 60 hours are preferred, more preferably from about 2 to about 12 hours. In a preferred embodiment, the mixture is loaded into a refractory crucible which is capable of withstanding the reaction temperature. An acceptable refractory will not react with the alkaline earth-manganese oxide composition, nor will it melt at the reaction temperature. The crucible can be heated in an electric or gas fired furnace or kiln, but any other method may be chosen if the method will heat the material to the necessary temperature for reaction. A peak temperature, as required by the composition, is preferably reached and maintained for a time as short as one half hour or as long as 16 hours or more. For example, a time of 4 to 6 hours may represent a good compromise between complete reaction and economy of manufacture. The calcination process may optionally include the loss or gain of oxygen in order to maintain electroneutrality.

[0034] After the starting oxides or compounds are mixed and heated or calcined, they are cooled, ground and dried if necessary. Grinding is typically required in order to reduce the particle size and finish of the pigment. An air mill is the preferred method of particle size reduction, but a pebble or ball mill, attrition mill or other type of grinding device may be used. After grinding, the alkaline earth-manganese oxide pigments preferably have average particle sizes of from about 0.1 to about 20 microns, more preferably from about 0.5 to about 5 microns.

[0035] As a particular example, to produce a strontium manganese oxide pigment of the formula SrMnO_y, 1 mol of manganese dioxide may be mixed with 1 mol of strontium oxide (as strontium carbonate) and calcined at 1,200°C for 4 hours. After cooling the material is charged in a pebble mill and ground to a particle size of 0.5 to 10 microns, preferably about 2.5 microns. The ground strontium-manganese oxide material is washed, dewatered, dried and dispersed. A black pigment with acceptably high infrared reflectance results. This process can be applied to other alkaline earth manganese oxide pigments, such as those listed in Table 6.

Table 6

Chemistry	Color	Mol alkaline earth per 1 mol Manganese	Calcine Temp.	IR Spectra
SrMnO _y	Black	1.0	1,200°C	Figs. 2 and 3
Ca ₂ MnO _y	Black	2.2	1,100°C	Figs. 2 and 3
Ca _{0.5} MnO _y	Red-Brown	0.5	1,200°C	Figs. 4 and 5
BaMnO _y	Yellow-Brown	1.0	1,100°C	Figs. 4 and 5
Sr ₂ MnO _y	Green	2.0	1,100°C	Figs. 6 and 7
Ba ₂ MnO _y	Green	1.8	1,100°C	Figs. 6 and 7

[0036] The alkaline earth-manganese oxide pigments of the present invention may be used in many applications such as automotive and marine paints, and colored plastics such as vinyl siding. One advantageous property in these applications is the high IR reflection exhibited by the pigments. This property allows the pigments to develop the desired color in the visible range, while reflecting a large amount of the IR radiation outside of this visible range. This means that the surface of objects colored with the present IR reflective pigments remain cooler under solar radiation than those not colored with IR reflective pigments. The reflectance properties of materials incorporating the present pigments are preferably higher at IR wavelengths compared to visible wavelengths (400-700 nm). The IR wavelengths include near-IR (700-2,000 nm), mid-IR (2,000-4,000 nm), and far-IR (4,000-5,500 nm). The use of the present alkaline earth-manganese oxide pigments may provide improved IR reflectance characteristics at some or all of these wavelengths. The alkaline earth manganese oxide pigments exhibit much less heat buildup and much higher infrared radiation reflectance in comparison to conventional colorants that yield a similar color.

[0037] Plastic, rubber, paint and other compositions incorporating the present pigments may possess improved IR reflectance properties. Also, various types of substrates may be coated with the present pigments, such as wood, glass, ceramic, metal, plastic and composite substrates to provide an organic coating or paint which provides improved IR reflectance and low heat buildup properties.

[0038] Figs. 2-7 illustrate improved IR reflectance characteristics achieved with the present alkaline earth-manganese pigments in comparison with conventional pigments. The masstone samples shown in Figs. 2, 4 and 6 were made and tested by adding 2g pigment to 70g polyvinyl carbide (PVC). The pigment was dispersed within the PVC at 420°F on a two-roll mill. The tint samples shown in Figs. 3, 5 and 7 were made and tested by adding 2g pigment to 70g PVC containing 10 wt% titania. The reflectance curves of these tint samples were measured to determine the relative strength of each pigment. A second series of tint samples were then prepared, adjusting the pigment loading such that each sample had a comparable strength, or value of reflection in the visible range.

[0039] As illustrated in Figs. 2-7, materials colored with the present alkaline earth-manganese oxide pigments have similar optical reflectance curves in the visible spectrum in comparison with conventional colorants, but possess markedly increased reflectance characteristics in the IR region at wavelengths up to 1,100 nm and higher. These reflectance characteristics are highly advantageous in applications where darker colors are preferred and heat buildup due to the absorption of IR radiation is to be minimized.

[0040] The alkaline earth-manganese oxide pigments of the present invention also preferably exhibit increased IR reflectances at wavelengths of up to 2,500 nm and higher, as demonstrated in Fig. 8. Specifically, Fig. 8 illustrates visible and infrared reflectance characteristics at wavelengths of up to 2,500 nm for Ca-Mn-O, Sr-Mn-O and Ca-Sr-Ba-Mn-O pigments of the present invention.

[0041] Pigments such as those shown in Figs. 2-8 with IR reflectances of, for example, greater than 50% at 1,100 nm will generally perform well in heat buildup tests. Thermal energy from solar radiation is absorbed at wavelengths of up to about 2,500 nm. Table 8 contains data for samples that were tested for heat buildup using ASTM Method 4803. The samples containing Sr-Mn-O, Ca-Mn-O and Ba-Mn-O black pigments of the present invention are more than 40°F cooler than conventional carbon black. There is a similar trend for the green pigments in which the present alkaline earth-manganate green pigments are all 40°F cooler than the conventional carbon black.

Table 8

Infrared Radiation Induced Heat Buildup			
Chemistry	Color	Max T (°F)	** Heat build-up (°F) Difference
Carbon Standard	Black	215.0	---
Sr-Mn	Black	159.4	-55.6
Ca-Mn	Black	171.1	-43.9
Ni-Mn-Cr-Fe	Black	190.2	-24.8
Co-Cr-Fe	Black	196.3	-18.7
Ca-Mn	Brown	164.7	-50.3
Sr-Mn	Green	164.6	-50.4
Ba-Mn	Green	171.2	-43.8
Co-Cr-Zn-Ti	Green	197.4	-17.6

* Samples run at 2.86 PPH

** Maximum Carbon Black Temp minus Maximum R&D Temp

[0042] As shown in Table 8, samples comprising the alkaline earth-manganese oxide pigments of the present invention exhibit substantially decreased heat buildup when subjected to IR radiation in comparison with commercially available carbon black, Ni-Mn-Cr-Fe, Co-Cr-Fe and Co-Cr-Zn-Ti pigments. The ability of the present pigments to reduce IR-induced heat buildup has particular significance for uses such as architectural, automotive, military, aerospace, industrial and electronics applications.

[0043] The pigments of the present invention may be used as colorants for various types of materials. Plastic or rubber compositions to which the alkaline earth-manganese oxide pigments may be added in accordance with this invention include polymeric materials that are natural or synthetic. Examples include natural resins, rubber, chlororubber, casein, oil-modified alkyd resins, viscose, cellulose acetate, cellulose propionate, cellulose acetobutyrate, nitrocellulose, or other cellulose ethers or esters. Synthetic organic polymers produce by polymerization, polyaddition, or polycondensation in thermosetting or thermoplastics can also be colored by this invention. Examples are polyethylene, polystyrene, polypropylene, polyisobutylene, polyvinylchloride, polyvinylacetate, polyacrylonitrile, poly acrylic acid, other polyolefins and substituted polyolefins, as well as methacrylic acid esters, butadiene, as well as copolymers of the above mentioned. Examples from polyaddition and polycondensation resins are the condensation products of formaldehyde with phenols, phenolic resins, urea, thiourea, and melamine, amino resins, polyesters, polyamides, polycarbonates, and/or silicones. These polymers can be present individually or as mixtures as plastic material or melts spun into fibers. They can also be dissolved as film formers or binders for lacquers, paints, or printing inks such as linseed oil, nitrocellulose, melamine resins, acrylic resins, ureaformaldehyde resins and the like.

[0044] The present alkaline earth-manganese oxide pigments may also be provided in liquid or paste form. Suitable liquid carriers for the alkaline earth-manganese oxide pigments include pine oils, vegetable oils, mineral oils, low molecular weight petroleum fractions, tridecyl alcohols, synthetic resins and natural resins. When used in paints for architectural, automotive, marine and other applications, the alkaline earth-manganese oxide pigment preferably comprises from about 0.1 to about 50 weight percent of the liquid paint composition, more preferably from about 1 to about 30 weight percent. For example, latex architectural paints preferably comprise from about 0.5 to about 50 weight percent of the alkaline earth-manganese oxide pigments, with the remainder of the paint comprising water, resin and solvents. Oil-based paints preferably comprise from about 0.5 to about 50 weight percent of the present alkaline earth-manganese oxide pigments, with the remainder comprising organic solvents, resins and additives.

[0045] The present pigments provide good colorant properties as well as several other advantages over conventional pigments. As described above, one of the reasons that the present alkaline earth manganese oxide pigments are advantageous is that their IR reflectance is higher than conventional pigments. Typical black or dark colored colorants for the plastics industry are based on either carbon black, hematite Cr-Fe based blacks, or spinel blacks formulated with Ni-Mn-Cu-Fe-Cr. In plastics applications with solar exposure, carbon black pigments absorb light not only in the visible range, but also into the infrared region. This leads to higher temperatures on the exposed color surface, which may cause additional energy costs, or premature failure or degradation of the exposed part. Conventional Cu-Cr oxide pigment compositions, which may contain other additives, do not perform much better than the carbon blacks.

[0046] Another advantage of the present alkaline earth manganese oxide pigments is based upon their chemistry. Typical colorants for the glass and ceramic industry may contain copper, nickel, cobalt or chromium in their formulations.

When glasses decorated with these pigments are recycled, the aforementioned elements impart objectionable color or physical properties to the recycled glass. Manganese and alkaline earth metals, on the other hand, do not impart such objectionable characteristics in recycled materials. Therefore, due to more stringent recycling efforts, these colorants may be used where traditional colorants are not suitable.

[0047] Furthermore, the present pigments are formed from low cost, easily obtainable starting materials, which makes them commercially attractive in comparison with conventional pigments such as cobalt and transition metal pigments currently in use.

[0048] Whereas particular embodiments of this invention have been described above for purposes of illustration, it will be evident to those skilled in the art that numerous variations of the details of the present invention may be made without departing from the invention as defined in the appended claims.

Claims

1. A pigment comprising alkaline earth-manganese oxide of the formula Me_xMnO_y , where Me is at least one metal selected from Ca, Sr, Ba and Mg, x is from 0.01 to 99, and y designates the number of oxygen atoms required to maintain electroneutrality.
2. The pigment of claim 1, wherein y is greater than or equal to x + 1 and less than or equal to x + 2.
3. The pigment of claim 1, wherein x is from 0.25 to 4.
4. The pigment of claim 1, wherein the alkaline earth-manganese oxide comprises Me_2MnO_4 , where Me is at least one metal selected from Ca, Sr and Ba.
5. The pigment of claim 1, further comprising at least one dopant including at least one element from Groups I-A, III-A, IV-A, V-A, VI-A, VII-A, VIII-A, I-B, II-B, III-B, IV-B, V-B, VI-B, VIII-B, the Lanthanide elements and the Actinide elements of the Periodic Table.
6. The pigment of claim 1, wherein the pigment exhibits an infrared reflectance of greater than 50 % and at least one wavelength of from 1100 nm to 2500 nm.
7. A coating composition comprising: a liquid carrier and a pigment comprising alkaline earth-manganese oxide of the formula Me_xMnO_y , where Me is at least one metal selected from Ca, Sr, Ba and Mg, x is from 0.01 to 99, and y designates the number of oxygen atoms required to maintain electroneutrality dispersed in the carrier.
8. The coating composition of claim 7, wherein the pigment comprises from about 0.1 to about 50 wt.-% of the coating composition.
9. The coating composition of claim 7, wherein the liquid carrier comprises at least one solvent selected from pine oils, vegetable oils, mineral oils, synthetic resins and natural resins.
10. The coating composition of claim 7, wherein the pigment is selected of a pigment of any of the claims 2 to 6.
11. An article comprising: a substrate matrix and a pigment comprising alkaline earth-manganese oxide of the formula Me_xMnO_y , where Me is at least one metal selected from Ca, Sr, Ba and Mg, x is from 0.01 to 99, and y designates the number of oxygen atoms required to maintain electroneutrality dispersed in the substrate matrix.
12. The article of claim 11, wherein the substrate matrix comprises plastic or rubber.
13. An article comprising: a substrate and a coating including a pigment comprising alkaline earth-manganese oxide of the formula Me_xMnO_y , where Me is at least one metal selected from Ca, Sr, Ba and Mg, x is from 0.01 to 99, and y designates the number of oxygen atoms required to maintain electroneutrality covering at least a portion of the substrate.
14. The article of claim 13, wherein the substrate comprises glass, ceramic, metal, plastic, carbon or composite.
15. A method of making an alkaline earth-manganese oxide pigment of the formula Me_xMnO_y , where Me is at least

one metal selected from Ca, Sr, Ba and Mg, x is from 0.01 to 99, and y designates the number of oxygen atoms required to maintain electroneutrality comprising: mixing powders of at least one oxide of an alkaline earth metal selected from Ca, Sr, Ba and Mg, or at least one compound capable of forming the at least one oxide, with manganese oxide, or at least one compound capable of forming manganese oxide so that Me and Mn are present in an ratio of x to 1 and calcining the mixture.

16. The method of claim 15, further comprising calcining the mixture at a temperature of from about 900 to 1300 °C.

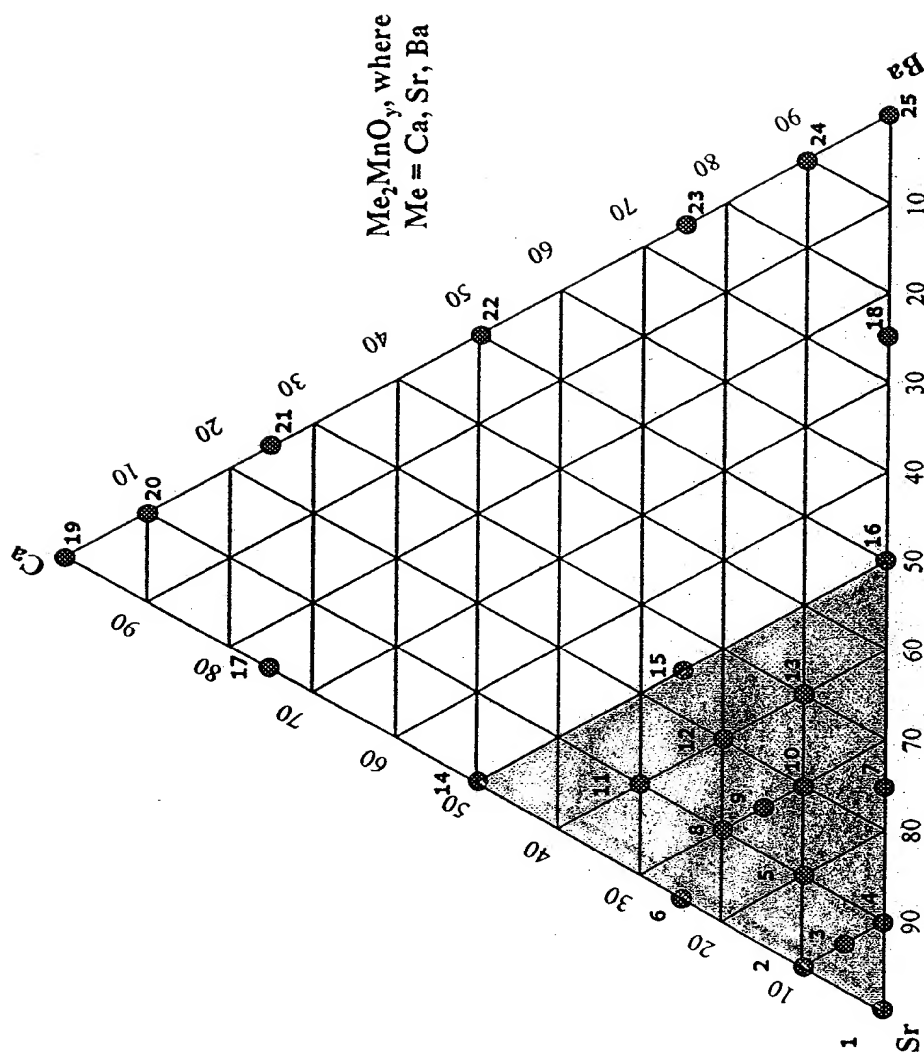


FIG. 1

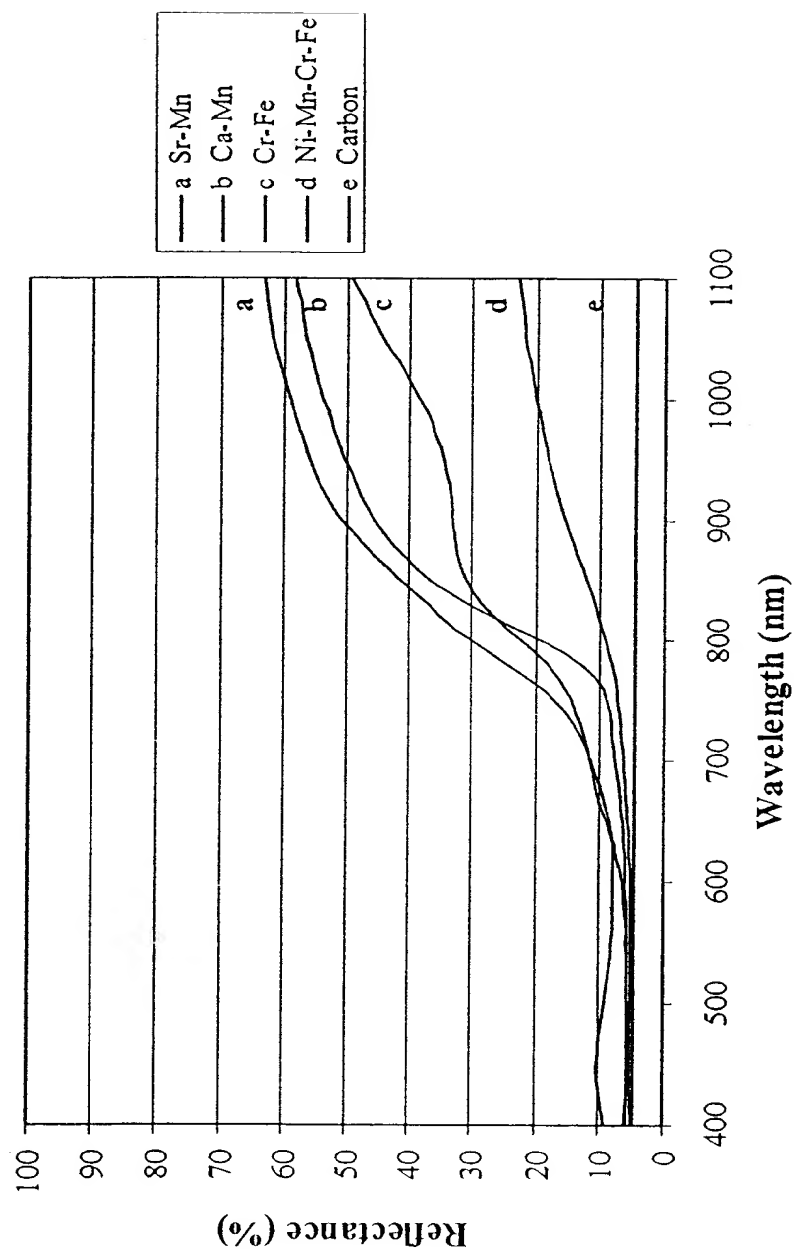


FIG. 2

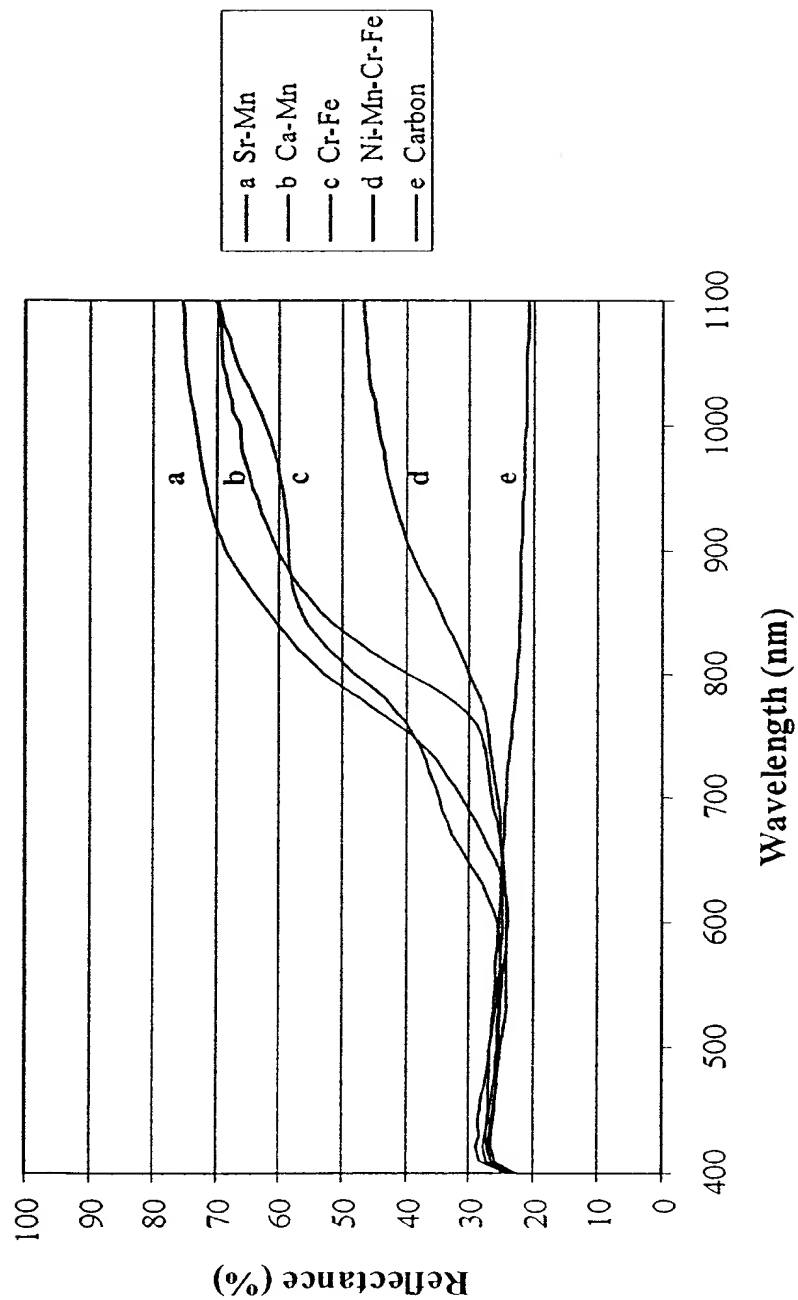


FIG. 3

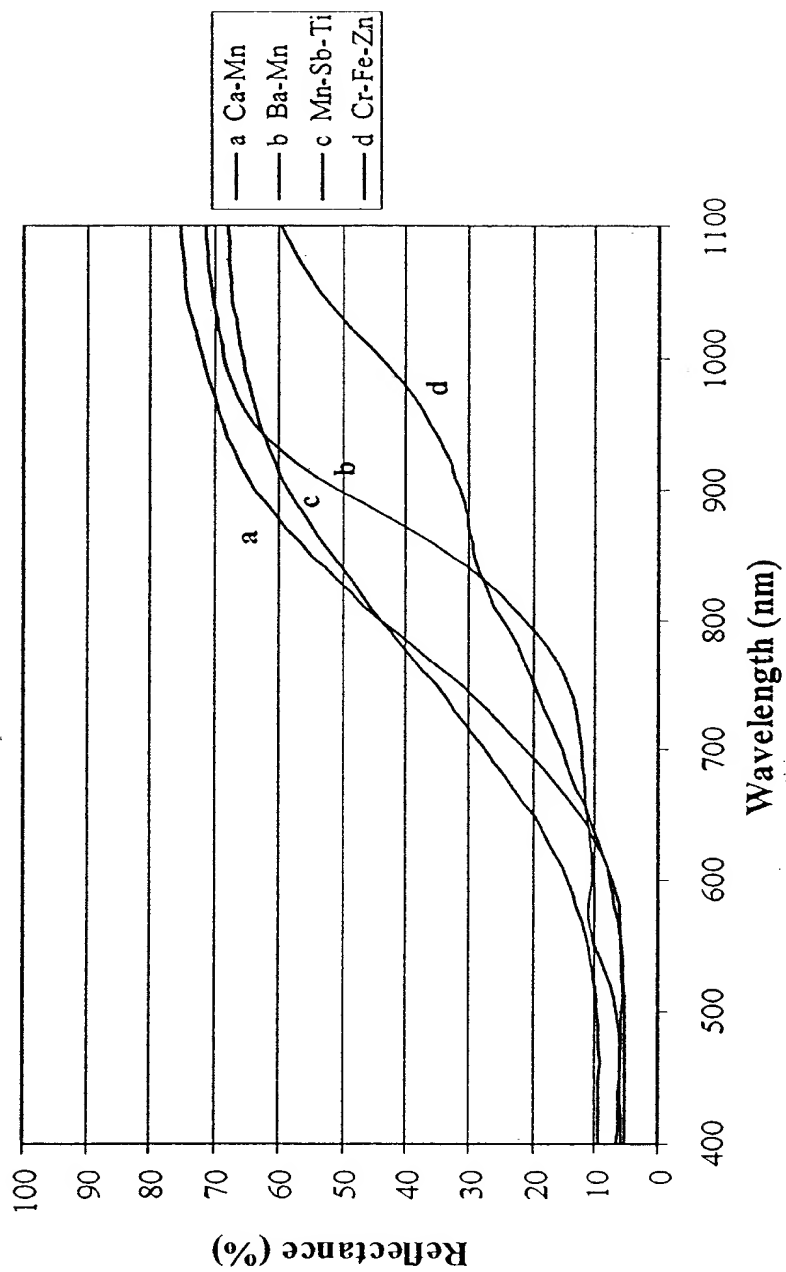


FIG. 4

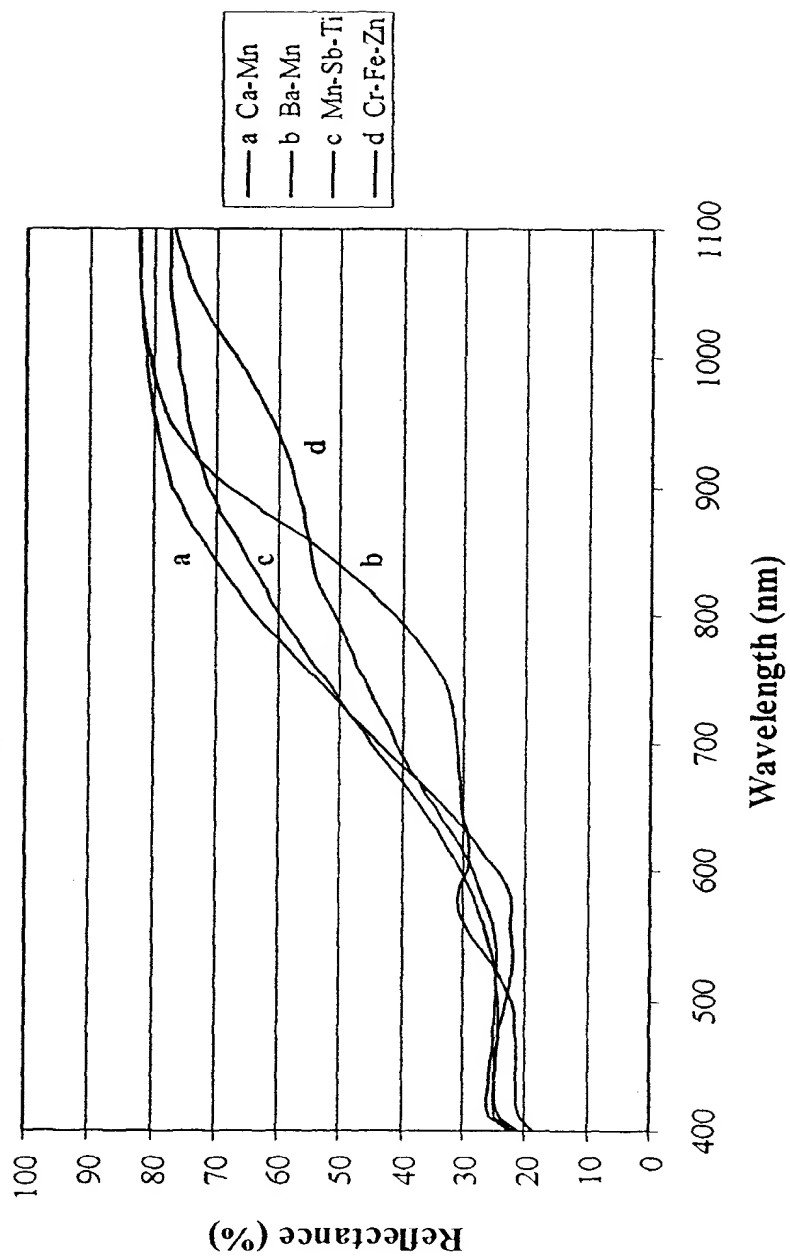


FIG. 5

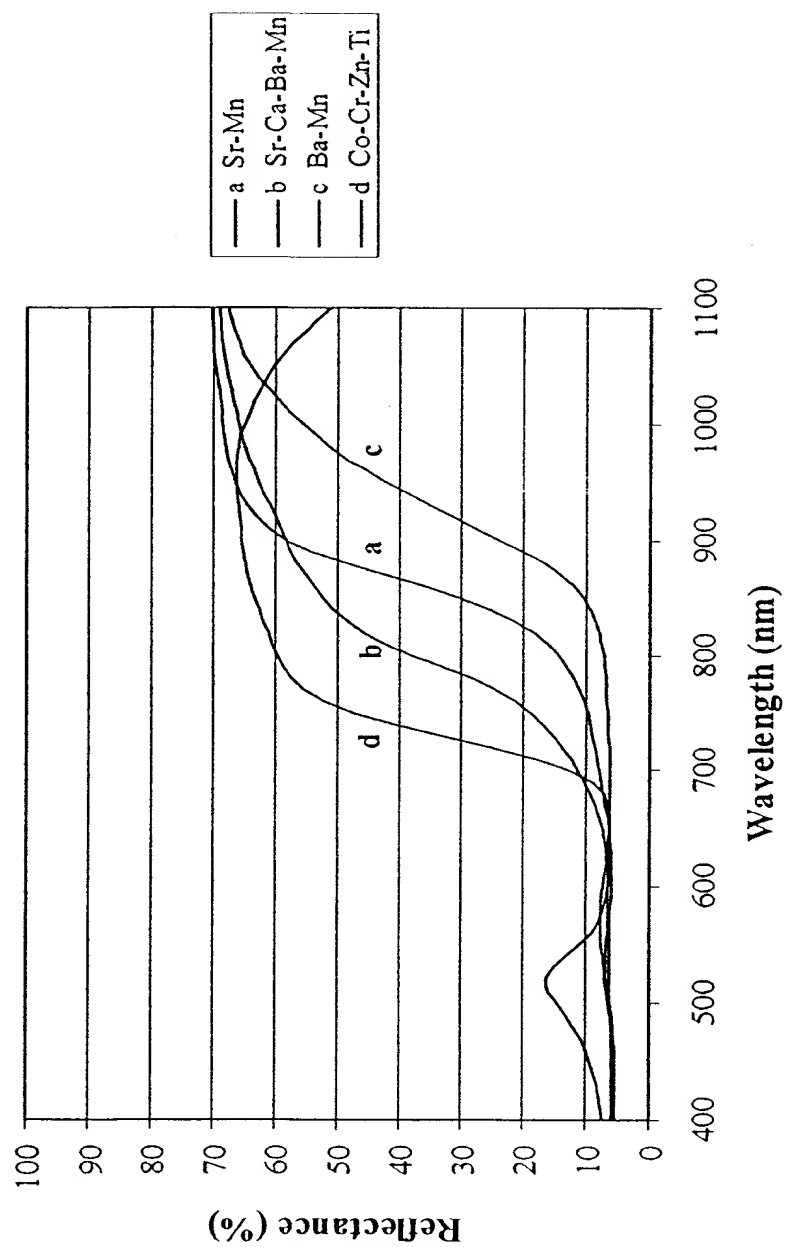


FIG. 6

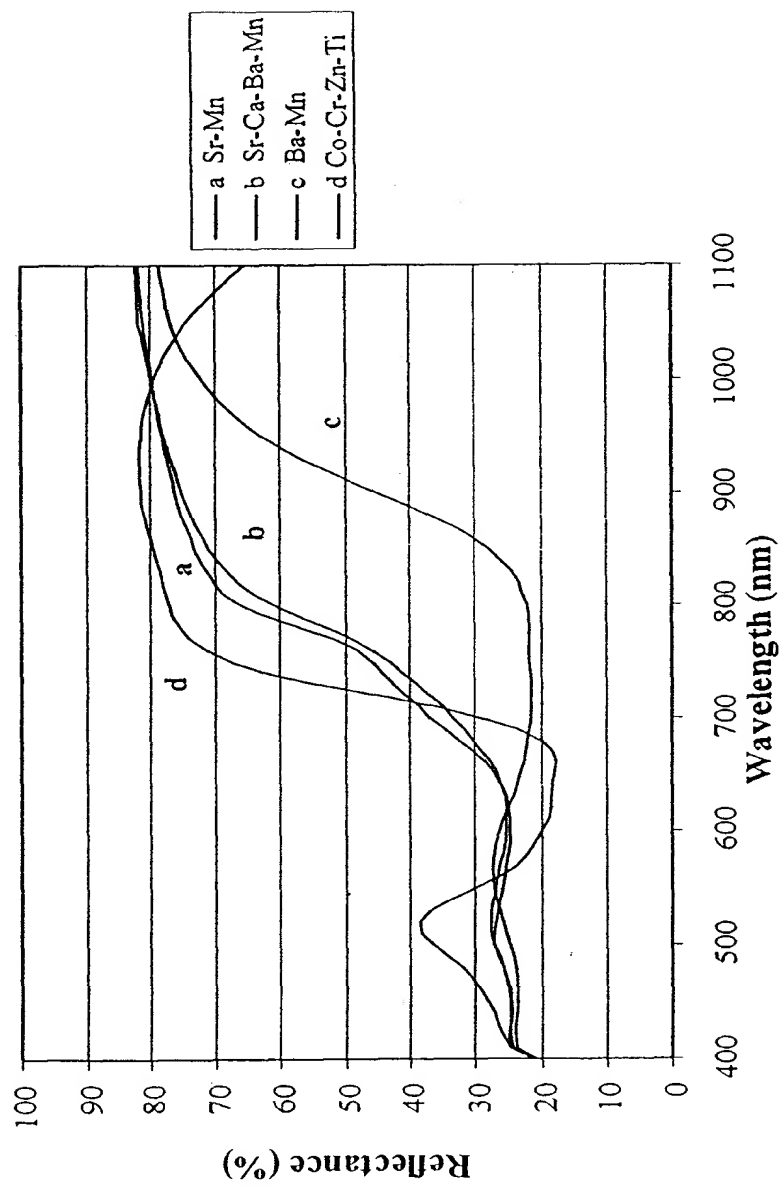


FIG. 7

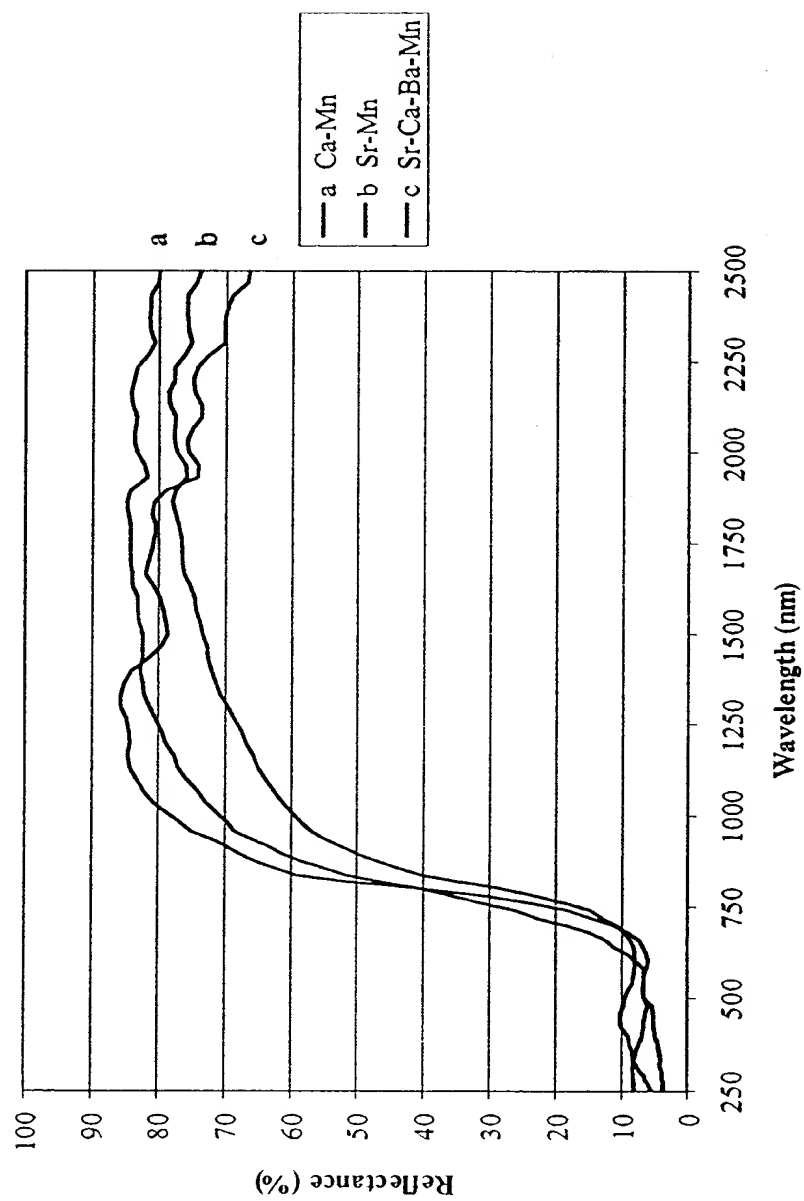


FIG. 8